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X-RAY STUDY OF THE STRUCTURE OF MOONSTONES

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1. Introduction

Moonstones which represent the potash-soda series of mixed feldspars lying in the compositional range Or_{85} Ab_{15} to Or_{40} Ab_{60}, exhibit a characteristic optical effect, commonly known as schiller. To all external appearances, they are monocrystals with symmetry elements characteristic of the monoclinic system. The optical phenomenon displayed by them, however, betray their complex nature, for the phenomenon arises due to optical heterogeneity of the medium. X-ray methods may therefore be expected to throw light with regard to the precise nature of the material responsible for the heterogeneity. Indeed, earlier X-ray investigations of Kozu and Endo (1921), Chao, Smare and Taylor (1939), Chao and Taylor (1940) and Ito (1950) have shown that moonstones possess a complex structure; the soda-feldspar having segregated as a distinct crystalline phase with triclinic symmetry, from the monoclinic potash-feldspar. The fact that the existence of the former feldspar as a separate phase is directly connected with the schiller phenomenon is shown by heat-treatment studies on moonstones. In recent years, X-ray studies by Mackenzie and Mackenzie and Smith (1955, 1956, 1958) on alkali feldspars have shown that there exist high and low temperature perthites. Further, the unmixed soda-phase has a considerable amount of potash feldspar in solid solution as is found from a^* and γ^* values of the former phase. All previous X-ray studies have established the fact that while the potash feldspar phase exist with monoclinic symmetry, the soda-feldspar crystallites in the moonstones have triclinic symmetry and are twinned either according to pericline or albite law. However, the explanations advanced with regard to the factor influencing the type of twinning assumed by the soda-feldspar crystallites are contradictory and have not provided the correct answer to this interesting question. Further, there are some points with regard to the structure of Korean Moonstones needing clarification, in view of the different interpretations given by Chao and Taylor on the one hand and by Ito on the other.

The optical effect exhibited by moonstones was investigated in great detail in this laboratory several years ago and an account of the same appeared

in these *Proceedings* (1950, 1953). The need for an independent X-ray investigation was keenly felt at that time to elucidate on the complex nature of moonstones whose optical behaviour was thoroughly understood. For various reasons such a study could not be carried out then. Recently another type of moonstone from the Coimbatore District in South India came to our notice which exhibits, apart from a golden yellow schiller, other highly characteristic optical effects, namely, polarised transmission and forward diffusion effects. Subsequent to our previous studies, a fair number of Korean moonstones exhibiting schiller were added to our collection. These circumstances and for the reasons already set forth, a thorough investigation by X-ray methods was undertaken recently on all the above-mentioned materials by single crystal methods. Of these, the Coimbatore moonstone is studied for the first time. As a precise investigation was called for, the Weissenberg method was extensively employed along with rotation methods. Both natural and heat-treated materials were studied and accurate measurements of the lattice constants were obtained. The results have greatly aided in putting forth an explanation for the differences in the twinning behaviour, based on the differences between the lattice constants of the constituent feldspar in moonstones. Further, the studies by the Weissenberg method have led to a determination of the precise nature of the crystallographic relationships of the two feldspars and the structural characters of the soda-feldspar phase. In this communication the results of the experimental study and the conclusions drawn from them would be set forth in detail.

2. Rotation Diagrams of Moonstones

In the oscillation and rotation photographs of all moonstones, two kinds of reflections are distinguishable; a set of strong, sharp reflections and a set of weak and somewhat diffuse ones. They evidently have different origin, the stronger ones arising due to the potash-feldspar phase and the latter due to soda-feldspar. Certain common features are noticeable in the X-ray rotation photographs of the three moonstones (Coimbatore, Ceylon and Korean varieties). The principal reflections in the *b*-axis rotation photographs are symmetrically disposed with respect to the zero layer, revealing thereby the presence of a symmetry plane perpendicular to that axis. The *a*-axis photographs of all moonstones examined consist of a double set of layer lines, one set comprising of strong reflections and another of weaker reflections. The latter are spaced wider than the former and the corresponding axes lie very nearly parallel. In every case, the morphological axes of the moonstone are found to coincide with the crystallographic axes of the potash feldspar phase.

The *b*- and *c*-axis rotation photographs divide these three moonstones into two types. In one type, while the X-ray photograph for the *c*-axis rotation exhibits features characteristic of a simple layer line diagram, the *b*-axis rotation photograph is complex. In the latter, strong reflections fall accurately upon layer lines and weak subsidiary reflections accompany these. In general, each principal reflection is accompanied by a pair of satellites, one lying above and the other below the layer line, on curves of constant ζ. The distribution of the subsidiary reflections is characteristic of an oscillation photograph with misset axes and their symmetrical appearance about the layer line indicates the presence of two such axes, equally inclined to the principal axis. In the second type, the position is reversed, namely, that while the *b*-axis rotation picture has the characteristics of a simple layer line diagram, the rotation diagram for the *c*-axis is complex. The distribution of the subsidiary reflections in the photograph is indicative of the existence of two subsidiary *c*-axes, symmetrically inclined to the principal axis.

To the first type belong the Ceylon and Coimbatore moonstones and to the second type the Korean variety. Figures 1 and 2 reproduce *b*-axis oscillation photographs of the Coimbatore and Korean moonstones respectively. In recording these, the crystal was oscillated through a range of 15° with (001) plane set parallel to the X-ray beam at the middle of the oscillation range (*see* Mackenzie and Smith, 1955). In the oscillation photograph of the Korean moonstone, the principal reflection can be seen accompanied by weaker subsidiary reflections. The features described for the Coimbatore and Ceylon moonstones are clearly to be seen in Fig. 1.

The foregoing facts become intelligible, if it is assumed that in all moonstones, the potash feldspar exists as a truly monoclinic component and that the soda-feldspar crystallites possess triclinic symmetry and are arranged in the mutual orientation characteristic of albite twin law in the case of Coimbatore and Ceylon moonstones, and in the orientation characteristic of the pericline twin law in the case of Korean moonstone.

3. Weissenberg X-Ray Diagrams

Zero layer Weissenberg photographs about *a*, *b* and *c* axes were recorded for all the varieties of moonstones, employing CuK_α radiation and a Unicam Weissenberg X-ray Goniometer.

a-axis.—In the *a*-axis photograph of the Coimbatore moonstone, two subsidiary reflections appear close to the principal ones from (*okl*) and (*ool*) planes, while in the case of Korean moonstones, the *oko* and *okl* spots are accompanied by two such reflections. Single spots appear for the *oko*

reflections in the former moonstone and for the *ool* reflections in the latter. The *a*-axis zero layer photograph of the two moonstones are reproduced in Figs. 3 and 4. In the photograph for the Korean moonstone the *oko* reflections apear as long streaks but these actually consist of three spots merging into each other. The triple character of the reflections can be seen in *okl* reflections.

b-axis.—In photographs for the Coimbatore moonstones, the principal reflections from the (*ool*) and (*hol*) planes have two close satellites and the corresponding reflections in the case of Korean moonstone consist of single and double spots. In both cases the *hoo* reflections are accompanied by single subsidiary reflections which lie more or less in the same line as the principal reflection.

c-axis.—In the *c*-axis zero layer photograph of the Coimbatore moonstone all the reflections except those from (*oko*) planes are doubled. But in the photographs for the Korean moonstone it is seen that the principal reflections from the (*hko*) and (*oko*) planes have two subsidiary reflections, the *hoo* reflections appearing doubled.

The X-ray photographs of Ceylon moonstones of both the blue and white schiller variety exhibit characters similar to that described for the Coimbatore variety. The differences in the features observable on the Weissenberg photographs arise due to the different twinning laws of the soda-feldspar phase. The two individuals of the albite twin have the (010) plane common and are related to each other by a rotation through 180° about the normal to this plane. While this operation leaves the b^* axes coincident, the c^* axes of the reciprocal lattice do not coincide and are symmetrically inclined with respect to the c^* axis of the monoclinic phase. Therefore planes involving l indices of the soda-feldspar have two points in the reciprocal lattice, giving rise to two subsidiary reflections. In the case of pericline twinning, the individuals are related by a rotation through 180° about the *b*-axis, which operation, while bringing the a^* and c^* axes into coincidence leave the b^* axes non-coincident. The latter are symmetrically inclined with respect to the b^* axis of the monoclinic phase. Now, the planes involving k indices are doubled and give rise to two subsidiary reflections. The (*hoo*) spacings differ for the two feldspars and therefore reflections from these are doubled.

A noteworthy feature observable on Weissenberg photographs is that only single spots appear from the triclinic soda-feldspar phase accompanying the principal reflections from (*hoo*) planes. This result leads to the important conclusion that the interaxial angle γ is very nearly equal to 90° for the soda-feldspar phase in these moonstones.

The zero and *n* layer Weissenberg photographs of the Korean moonstone rotated about the *b*-axis reveal that a monoclinic potash phase and a pericline twinned soda-phase coexist in it. No evidence for the presence either of a triclinic potash phase or monoclinic soda-phase could be found in the photographs. This is in agreement with the results obtained by Chao and Taylor (*loc. cit.*) for Korean moonstone.

4. X-Ray Patterns of Heat-treated Moonstones

When moonstones are heated to about 850° for a few hours, the schiller vanishes. This fact was reported earlier by E. Spencer (*loc. cit*). Some of the heat-treated specimens were examined by Taylor and collaborators (*loc. cit.*).

In the present series of studies, the moonstones were heat-treated, and their X-ray patterns were recorded both by rotation and Weissenberg methods. The heat-treatment was carried out at 900° C. for about three hours and the specimens were then allowed to cool to room temperature. In X-ray photographs of heat-treated moonstones, all subsidiary reflections characteristic of the untreated material vanish. The detailed characteristics of the rotation diagrams which consist of single set of layer lines, and the Weissenberg photographs reveal that the heat treated material possess monoclinic symmetry. The lattice constants of the heat-treated moonstones were obtained from a measurement of the high-order reflections in the respective Weissenberg photographs and are presented in Table I along with the data for the potash-feldspar phase of the untreated material.

Table I

Lattice Constants of Natural and Heat-treated Moonstones in A.U.

Lattis Constant	Coimbatore moonstone		Ceylon moonstone		Korean moonstone	
	Natural	Heat-treated	Natural	Heat-treated	Natural	Heat-treated
a^*	7·70	7·58	7·72	7·619	7·63	7·50
b^*	12·94	12·94	12·84	12·84	12·94	12·94
c^*	6·40	6·42	6·42	6·45	6·39	6·40
a	8·57	8·46	8·59	8·47	8·49	8·34
b	12·94	12·94	12·84	12·84	12·94	12·96
c	7·20	7·14	7·17	7·17	7·12	7·13

It will be seen from a scrutiny of the data presented in the table that a significant contraction along the *a*-axial dimension has taken place on heat-treatment. This change is found to be proportional to the amount of soda-feldspar that has gone into solution. In estimating the contraction, the value for the natural material should be taken as 8·61 Å which is the value for pure orthoclase. If a certain percentage of soda-feldspar has already gone into solution in the potash phase of the untreated material, the actual value for the latter would be brought down. This is what has happened in the case of Korean moonstone. The difference in the *a*-axial dimension between heat-treated Korean moonstone and orthoclase is nearly double that of such differences for the other two moonstones, as is to be expected, in view of the higher percentage of soda-feldspar present in it, nearly 60% as against 30 to 33% in the others.

5. DISCUSSION OF THE RESULTS

The results obtained raise the interesting question, namely, what is the factor that is responsible for the soda-feldspar crystallites in the moonstones assuming a orientation characteristic of albite law in one case and pericline law in the other. Chao and Taylor (*loc. cit*) classified Spencer's specimens into two groups; those having albite twinned soda-phase whose lattice angles were close to low-albite, and those having pericline twinned soda-phase whose lattice angles did not agree with low-albite. They were not aware of the existence of high albite at that time which was proved beyond doubt by Tuttle and Bowen (1950), and gave a tentative explanation for this difference based on bulk chemical composition. Ito and Sadanaga (1952) put forward a similar suggestion. Laves (1952) thought that the type of twinning was controlled, depending upon whether the soda-phase has low or high albite structure. This suggestion was however contradicted by Smith and Mackenzie (1954).

Table II presents the *a*-axial dimensions of the potash phase and the lattice angles α^* and γ^* of the soda-feldspar phase for the three moonstones studied. The latter were obtained from measurements on Weissenberg photographs. The lattice angles for low albite are also given in the last column.

Mackenzie and Smith have shown that from the α^* and γ^* values of the soda-phase, the chemical composition of that phase could be determined. As remarked earlier, the present investigation shows that the composition of the monoclinic potash phase is revealed by the *a*-axial dimension of that phase. The *a*-axial dimension of the Korean moonstone whose bulk chemical composition is $Or_{40}\,Ab_{60}$ indicates that the potash phase in it holds an appreciable proportion of soda-feldspar, amounting to nearly 25 to 30% in so lid

TABLE II

Phase	Lattice constant	Korean moonstone	Ceylon moonstone	Coimbatore moonstone	Albite
Potash ..	a	8·49Å	8·59Å	8·57Å	..
Soda ..	α^*	88° 30′	86° 30′	87° 24′	86° 24′
Soda ..	γ^*	90°	90° 20′	90° 20′	90° 29′

solution. The α^* and γ^* values of the soda-phase in the same moonstone correspond to a chemical composition $Or_{30}\,Ab_{70}$.

It will be seen from Table II that in the case of Korean moonstones, the differences in respect of both the a-axial dimensions and the lattice angles α^* and γ^* between the two constituent feldspars are lessened, this essentially arising out of solid solution of an appreciable proportion of one phase in the other. Such circumstances favour pericline twinning of the soda-phase. On the contrary, these differences are greater in the case of Coimbatore and Ceylon moonstones and the two feldspar phases are very close to orthoclase and low-albite. When the soda-feldspar phase thus demands full-triclinic symmetry of low-albite and the a-axial dimension of the potash phase correspond to that of orthoclase, twinning takes after the albite law. The principal factor that seems to influence the nature of twinning is therefore the narrowing down of the differences in respect of the a-axial dimension of the two feldspars.

In conclusion the author wishes to express his sincere thanks to Sir C. V. Raman, F.R.S., N.L., for his kind interest in this work.

SUMMARY

X-ray studies on three different types of moonstones, namely, Ceylon, Coimbatore and Korean varieties have been made by single crystal rotation and Weissenberg methods. The results are consistent with the explanation that the triclinic soda-feldspar crystallites which has segregated out of monoclinic potash feldspar are twinned according to albite law, in the former two, while the twinning is according to pericline law in the latter moonstone. The view is put forward that the narrowing down of the differences, firstly of the a-axial dimension between the soda-feldspar and potash feldspar phases, and secondly between the lattice angles of the two feldspars result in pericline

twinning of the soda-phase, while albite twinning results when the soda-phase demands full triclinic symmetry and the potash phase has the a-axial dimension corresponding to that of orthoclase. The detailed features of the Weissenberg X-ray diagrams of Korean moonstones reveal that there exist in it a monoclinic potash phase and a pericline twinned triclinic soda-phase, in agreement with the results obtained by Chao and Taylor. X-ray results also indicate that the lattice angle γ of the triclinic soda-phase in these moonstones is very nearly equal to 90°.

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EXPLANATION OF PLATES

PLATE VI

FIG. 1. *b*-axis oscillation photograph of Coimbatore moonstone, oscillated through a range of 15° with the (001) plane in the middle of the oscillation range. Fainter reflections can be seen accompanying many of the spots. The (242) reflection is enclosed in square brackets and the subsidiary reflections can be seen, one on either side of the layer line.

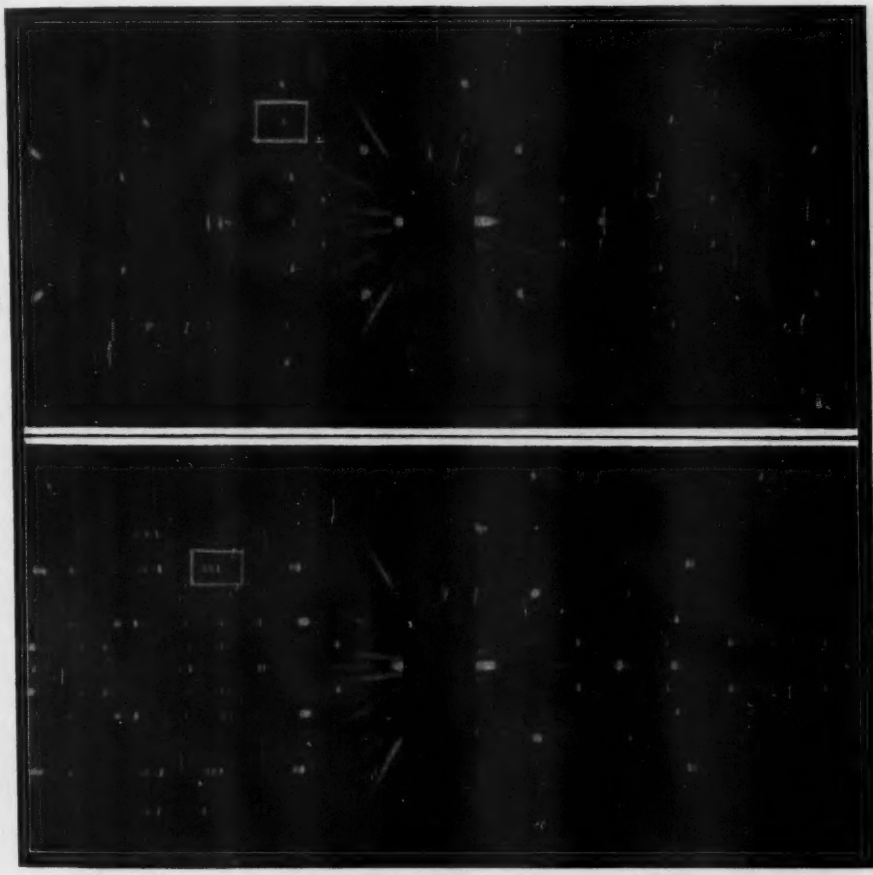

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 2. Same oscillation photograph as Fig. 1 with Korean moonstone. Principal reflections are accompanied by subsidiary reflection, but the latter fall in the layer line. The (442) reflection is enclosed in square brackets. The two subsidiary reflections can be seen on the left.

PLATE VII

FIG. 3. *a*-axis zero layer Weissenberg photograph of the Korean moonstones. The 001 and 010 reflections are marked. The triple character of the 010 reflections can be seen clearly on high angle spots.

FIG. 4. Same as Fig. 3, but with Coimbatore moonstone. The tripling of the 001 reflections can be clearly seen in the photograph.

SEPARATION OF URANIUM FROM IRON AND VANADIUM

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The photolytic separation of uranium from thorium, cerium, lanthanum and aluminium utilising sunlight has been reported earlier.[1] Uranium is precipitated as hydrated ammonium uranium (IV) fluoride[2] ($NH_4F \cdot UF_4 \cdot H_2O$) while the elements mentioned above remain in solution. The same method has been extended for the separation of uranium from iron and vanadium. In these cases, however, the adjustment of pH is of importance as otherwise uranium precipitated contains iron and vanadium as impurities. Experiments were, therefore, carried out at different pH values. Solutions having pH values between 2·0–2·5 have been found to precipitate uranium of high purity on photolysis. The composition of alcohol greatly affects the percentage of recovery of uranium. In both the cases 30% composition by volume of alcohol has been found to give the maximum yield 93·5%.

Experimental

Uranium nitrate, ferric nitrate used were of E. Merck, E.P. and G.R. quality respectively. Vanadyl formate prepared in our laboratory was used. Stock solutions of uranyl nitrate, ferric nitrate containing nitric acid and vanadyl formate also containing nitric acid for preventing hydrolysis were prepared.

Solution mixtures of uranyl nitrate and ferric nitrate of known U_3O_8 and Fe_2O_3 contents were prepared. To the mixtures of the solution 2·5 gm. of ammonium bifluoride ($NH_4F \cdot HF$) was added, after which the pH adjustment was made, using ammonia and nitric acid for the purpose. After this adjustment, required quantity of alcohol was added and the volume was made up to 150 c.c. It has been found that addition of alcohol changes the pH by 0·1 unit. Thus a series of mixtures having different pH values and different alcoholic compositions were prepared.

In case of preparing mixture of uranium and vanadium, the same procedure as described above was followed except that the mixture of solution

of uranyl nitrate and vanadyl formate containing nitric acid was first evaporated to a small volume with a view to convert the vanadyl formate to nitrate and eliminate excess of nitric acid. In this process much of the vanadium was precipitated. To the small volume of solution and precipitate obtained, 50 c.c. of water were added. The precipitate was removed by filtration thus allowing the filtrate to contain the uranium taken originally along with a part of the vanadium. The adjustment of pH and the addition of alcohol were carried out as described before, the entire volume of the solution being 150 c.c.

The solutions thus prepared were next exposed to bright sunlight in conical flasks. On exposure for a period of about 4–5 hours, the uranium precipitated as hydrated fluoride complex. The supernatant liquid when iron was present appeared almost colourless after photolysis, but when vanadium was taken the supernatant liquid turned deep blue although the original solution was of yellow colour.

The precipitate of hydrated ammonium uranium fluoride thus formed was filtered and washed with 10% alcoholic solution. On boiling the precipitate with ammonia the residue formed was filtered and ignited to oxide which was weighed. This oxide was then dissolved in dilute nitric acid and made up to a definite volume. Colorimetric determination of iron[3] was performed at this stage in order to ascertain if iron was present only in traces. In these cases when appreciable quantity of iron was present, the estimation of uranium was carried out by the method of Katz and Rabinovitch[4] as applied by Krishnaprasad and Dadape.[5]

In case of mixture of uranium and vanadium the colorimetric test[6] of the solution indicated that, if at all vanadium was present, it was in traces and therefore no further analysis was necessary. These colorimetric estimations of iron and vanadium were performed against blank solutions containing requisite amount of uranium only.

The composition of the solution taken in terms of U_3O_8, Fe_2O_3 and V_2O_5 in mg., the pH values of the solution-mixtures, the composition of alcohol by volume, the percentage of recovery and the percentage of purity of the product obtained by photolysis have been recorded in Tables I, II, III and IV.

It can be seen from Table I that at pH 3·5 the uranium recovered contained iron as impurity up to 3%, while at pH value 3·0 the impurity was 1·5%. At lower pH range 2·0–2·5, it was found that iron if at all present as impurity did not exceed 0·1%. Thus the adjustment pH in case of the separation of uranium from iron is of the utmost importance.

TABLE I

Separation of uranium from iron

With variation of pH

Weight in mg.

Composition of the mixture of nitrates calculated as oxides		pH value of the solution mixture	Composition of alcohol by volume	Ignition value of the product obtained by photolysis calculated as U_3O_8	% of recovery	% of purity
U_3O_8	Fe_2O_3					
471·5	125·0	2·00	10	411·8	87·35	99·9
471·5	125·0	2·30	10	413·0	87·60	99·9
471·5	125·0	2·90	10	419·5	88·96	98·68
471·5	125·0	2·04	20	435·7	92·41	99·9
471·5	125·0	2·46	20	438·6	93·03	99·9
471·5	125·0	2·95	20	445·3	94·45	98·5
471·5	125·0	3·50	20	453·3	96·14	97·1

TABLE II

Separation of uranium from iron

With variation of alcoholic composition

Weight in mg.

Composition of the mixture of nitrates calculated as oxides		pH value of the solution mixture	Composition of alcohol by volume	Ignition value of the product obtained by photolysis calculated as U_3O_8	% of recovery	% of purity
U_3O_8	Fe_2O_8					
471·5	125·0	2·50	10	415·9	88·18	99·9
471·5	125·0	2·42	20	438·7	93·05	99·9
471·5	125·0	2·40	30	439·6	93·24	99·9
471·5	125·0	2·38	40	441·0	93·53	99·9
471·5	125·0	2·35	50	443·0	93·96	99·9

TABLE III

Separation of uranium from vanadium

With variation of pH
Weight in mg.

Composition of the mixture of nitrates calculated as oxides		pH value of the solution mixture	Composition of alcohol by volume	Ignition value of the product obtained by photolysis calculated as U_3O_8	% of recovery	% of purity
U_3O_8	V_2O_5					
468·4	427·1	2·04	20	410·2	87·6	99·9
468·4	427·1	2·50	20	423·8	90·5	99·9
468·4	427·1	2·98	20	441·2	94·2	98·9

TABLE IV

Separation of uranium from vanadium

With variation of alcoholic composition
Weight in mg.

Composition of the mixture of nitrates calculated as oxides		pH value of the solution mixture	Composition of alcohol by volume	Ignition value of the product obtained by photolysis calculated as U_3O_8	% of recovery	% of purity
U_3O_8	V_2O_5					
500·0	439·2	2·50	10	428·0	85·6	99·9
500·0	439·2	2·44	20	448·2	89·8	99·9
500·0	439·2	2·48	30	465·1	93·0	99·9
500·0	439·2	2·52	40	468·5	93·7	99·9
500·0	439·2	2·46	50	469·9	94·0	99·9

In case of the mixture of uranium and vanadium, the pH range of the solution was, therefore, fixed within 2·0–2·5. The determination of

vanadium in traces by colorimetric method (*loc. cit.*) indicated in these cases that the percentage of impurity of vanadium if at all present would not exceed 0·1%.

This photolytic method has been applied to the separation of uranium from titanium and molybdenum and this will be published in due course.

SUMMARY

The separation of uranium from iron and from vanadium has been carried out, by photolysis utilising sunlight. For this purpose the mixture of the solutions of uranium and iron or vanadium with ammonium bifluoride containing different percentage of alcohol was exposed to sunlight for 4–5 hours. Uranium precipitated in the form of a hydrated complex fluoride, leaving iron and vanadium in the solution phase. Uranium of at least 99·9% purity, this being the limit of our detection by colorimetric method, was obtained on photolysing solutions having pH range between 2·0–2·5. The important factor for the percentage of recovery is the composition of the solution and it has been found that with 30% of alcohol the yield comes to about 93·5%.

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ULTRASONIC VELOCITIES IN RELATION TO THE DEGREE OF METAMORPHISM IN LIMESTONES

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1. Introduction

During the course of a detailed investigation on physical properties of rocks and their relation to certain geological features, the author has come across interesting results. It has been observed (1955, 1959) that ultrasonic velocities in rocks depend on granular texture (grain size, density and closeness of packing); dimensional orientation of crystallites composing the polycrystalline aggregate (rock); and their geological history. That the geological history has a considerable influence on the elastic properties of rocks has been brought out in detail in another paper by the author (1959). Geological history includes the various changes the rock had undergone during its lifetime. One such important change limestones are usually subjected to is the metamorphism. In the present investigation, a number of limestones have been examined under the microscope in order to study their granular texture and consequently the possible geological history to which the specimen has been subjected to. The effect of degree of metamorphism on the ultrasonic velocities in limestones has been investigated, in conjunction with its granular texture. Limestones are best suited for such studies, since they are monomineralic and various stages in their metamorphism are readily discernible. As anisotropy was noticed by the author (1959) in bedded limestones, massive limestones have been chosen for determining ultrasonic velocities in the present investigation. Number of specimens from same localities are chosen in order to confirm the values of velocities as far as the order is concerned and also to get a statistical value.

2. Experimental Results

The longitudinal (V_L) and torsional (V_T) ultrasononic velocities have been measured in a number of Indian limestones employing the total internal reflection method as described by Krishnamurthi and Balakrishna (1953). The velocities in kilometres/sec., together with densities (ρ) in gm./c.c. are given in Table I.

TABLE I

Ultrasonic Velocities in Limestones

Sl. No.	Locality		ρ	V_L	V_T
1	Manditog	..	2·72	7·27	3·50
2	Manditog	..	2·68	7·00	2·97
3	Manditog	..	2·65	6·68	3·06
4	Makrana	..	2·72	7·11	2·66
5	Ramagundam	..	2·80	7·07	3·40
6	Madhya Pradesh	..	2·86	6·24	3·02
7	Madhya Pradesh	..	2·80	6·26	3·07
8	Cuddapah	..	2·84	6·40	3·20
9	Cuddapah	..	2·66	5·89	2·94
10	Piduguralla	..	2·84	6·36	3·16
11	Piduguralla	..	2·74	6·56	3·12
12	Shahabad	..	2·68	6·15	3·00
13	Shahabad	..	2·68	5·97	3·71
14	Shahabad	..	2·68	5·94	3·50
15	Shahabad	..	2·68	5·83	3·62

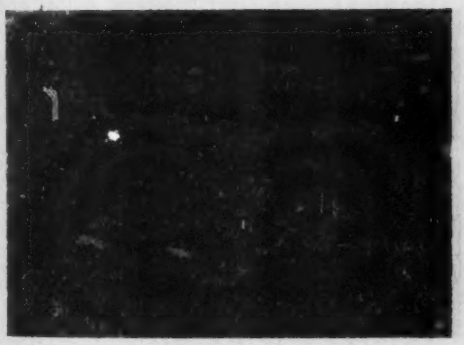
3. DISCUSSION

Specimens 1 to 3 are metamorphosed limestones which are marbles. The rest are limestones. Microscopic examination of marbles shows that they are recrystallised, reoriented and well compacted; in contrast to limestones which are sedimentary rocks and consequently porous and less compacted. It can be seen from Table I that the high degree of metamorphism to which the marbles have been subjected to, is reflected in the higher velocity values which they show in comparison with limestones which have not been subjected to any metamorphism whatsoever.

PHOTOMICROGRAPHS OF LIMESTONES

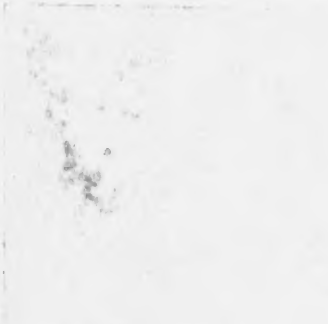
SPECIMEN 1, ×50

SPECIMEN 3, ×50



SPECIMEN 9, ×50

SPECIMEN 5, ×30



Another significant feature is in regard to limestone Specimen Nos. 4 and 5. The ultrasonic velocities exhibited by these limestones are comparable to those found in marbles. Even though they have not been metamorphosed, these specimens are characterised by fine grain and closeness of packing, features which enable them behave like marbles. In fact, photomicrograph of Specimen 5 in Plate VIII shows its fine grain texture very clearly.

Specimens 1, 3 and 9 represent various stages of metamorphism to which limestones have been subjected. Photomicrographs of these specimens in Plate VIII, further exemplify this fact. Specimen 1 is completely recrystallised and reoriented and consequently represents a high degree of metamorphism. Specimen 3 is partly crystallised and still ground mass can be seen clearly, thereby illustrating an intermediate stage of metamorphism. Specimen 9 is an unmetamorphosed massive limestone. These microscopic observations coupled with their respective velocity values in Table I suggest that velocity increases in a limestone as it reaches an advanced stage of metamorphism. In other words, the degree of metamorphism has an influence on the velocity values in a limestone. The higher the degree of metamorphism to which a limestone is subjected to, the higher velocity values it exhibits.

As observed in the earlier investigations in the case of quartzites and marbles, in the present investigation also it is noticed that in fine-grained rocks the velocity values are high and absorption low, while in coarse-grained rocks the velocity values are low and absorption high.

4. Conclusion

It can be concluded that metamorphosed limestones or marbles show higher ultrasonic velocity values in contrast to limestones. In limestones, velocity values consequential to the degree of metamorphism to which they have been subjected to are noticed and in fact the velocity increases as metamorphism increases. Certain chosen limestones, though not metamorphosed, behave like marbles and show comparable velocities because of their fine grain texture.

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CHEMICAL EXAMINATION OF THE LEAVES OF *RHODODENDRON NILAGIRICUM* ZENK.

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Plants belonging to the genus Rhododendron are considered to be poisonous to cattle.[1] The results of the chemical examination of the leaves of *Rhododendron falconeri* Hook. have been reported in an earlier communication from these laboratories.[2] *Rhododendron nilagiricum* Zenk. (Syn. *R. arboreum* Sm. var. *nilagirica* Cl.) grows abundantly in the Nilgiri Hills.[3] Wehmer reports that the species *R. arboreum* Sm. is poisonous and probably contains the glucoside ericolin[4]; but there is no reference in the published literature to past chemical work on the *nilagirica* variety. The results of the chemical examination of the leaves of this plant are described in the present paper.

The dried leaf material was subjected to two different extraction procedures in separate batches. In one procedure the leaf powder was extracted directly with alcohol. During concentration a large quantity of resinous matter separated, from which by suitable manipulation as described in the experimental portion, ursolic acid and epifriedelinol were obtained. From the resin-free alcoholic solution, hyperoside (3-D-galactoside of quercetin) was obtained along with some free quercetin.

In the second extraction procedure, the leaf powder was extracted first with ether and then with alcohol. Essentially the same crystalline components, *viz.*, ursolic acid, epifriedelinol and quercetin, were obtained; the isolation of the glycoside was given up in this extraction procedure, in view of the tedious nature of the procedural details (*see* experimental).

Ursolic acid was identified through its physical properties and preparation of its acetate (m.p. and mixed m.p. with an authentic sample).

Epifriedelinol is a triterpenoid compound of rather limited occurrence and has been reported to occur in *Ceratopetalum apetalum* D.Don.,[5,7] *Cetrania nivalis*[6,7] and *Prunus nepalensis* Koch.[8] The identity of epifriedelinol obtained in the present investigation was deduced from the colour reactions and the m.p., optical rotation and the analysis of the parent compound, of its acetate and its benzoate.

The identity of quercetin was deduced from its m.p., colour reactions and its acetate (m.p. and mixed m.p. with an authentic sample).

Hyperin was the name given to a glycoside first isolated from *Hypericum perforatum* L.[9] and reported to be the 3-α-D-galactoside of quercetin. The name hyperoside was suggested as more appropriate for it by Casparis *et al.*[10] Hyperoside has been shown to occur in many species belonging to the plant families Betulaceæ and Polygonaceæ, in a few cases by preparative methods, but more largely by paper chromatographic methods.[11–14] Hörhammer *et al.* have summarised the available information on the occurrence of hyperoside and of the closely related glycosides quercitrin and rutin.[13, 14] Quercetin-3-galactoside has also been reported to occur in the skins of Grimes Golden and Jonathan apples.[15]

The identity of the glycoside isolated in the present investigation as hyperoside has been established by its m.p., analysis and optical rotation, preparation of its acetate and its methyl ether, hydrolysis to quercetin and galactose and the hydrolysis of the methyl ether to 5 : 7 : 3′ : 4′-O-tetramethyl-quercetin (m.p. and mixed m.p. with an authentic sample). The nature of the sugar in the original glycoside was established by the preparation of its osazone and by paper chromatography.

Experimental

The material used in this investigation was obtained from Ootacamund, Nilgiri Hills in S. India.

First extraction procedure

The air-dried leaf powder (4 kg.) was extracted with cold methylated spirit repeatedly. The total extract (70 litres) was concentrated under reduced pressure to 4 litres, the solid separating being removed from time to time. Dilution with water and further concentration yielded some more solid. The combined solids (180 g.) and the clear aqueous-alcoholic solution (referred to again as solution X) were examined separately.

The solid was dissolved in methanol-benzene (1 : 1) (3 litres), filtered and diluted with enough water to lead to the separation of two layers. After separation of the layers, the aqueous methanol layer was extracted with ether (3 × 500 ml.) and the ether phase was added to the benzene phase. The combined benzene-ether solution (*ca.* 3 litres) was shaken with 5% aqueous sodium hydroxide solution (2 × 500 ml.) when a copious solid separated at the interphase. The filtered alkaline solution, the organic solvent layer and the floating solid were examined separately as below.

The alkaline solution, on acidification and ether extraction yielded on promising residue.

The filtered solid was dissolved in hot methanol, cooled and decomposed with excess of mineral acid. The precipitate obtained was purified by crystallization from alcohol, giving colourless needles, m.p. 280–82° (ursolic acid).

The benzene-ether solution was evaporated to remove the solvents and the residue partitioned between 90% acetic acid and petroleum ether, employing 300 ml., 30 ml., 30 ml. and 30 ml. portions of the former and 1 litre, 100 ml., 100 ml. and 100 ml. portions of the latter solvent. The united petroleum ether solution was washed neutral, dried and concentrated to a low volume (250 ml.), when a greenish solid (0·9 g.) separated. This on two crystallizations from chloroform yielded stout needles, m.p. 280–81° (epifriedelinol). The mother liquor yielded a resinous solid (84 g.) on complete removal of the solvent; this was not examined further.

No worthwhile residue was obtained from the acetic acid layer on dilution with water and extraction with ether.

The residual aqueous-alcoholic extract of the original leaf (solution X, *see* earlier) was extracted with ether (10×400 ml.) containing 3% alcohol. The united ether solution was concentrated with occasional addition of water and the remaining aqueous solution was extracted with *iso*-amyl alcohol (5×200 ml.). The united amyl alcohol extract was concentrated to 100 ml. and poured with stirring into a large excess of petroleum ether. The precipitated solid was filtered (42 g.) and extracted with hot water repeatedly (10×200 ml.). The aqueous extract was concentrated under reduced pressure to a syrupy consistency and the residue was taken in absolute alcohol and left in the ice-chest when a fine yellowish powder separated after a week (0·6 g.) (hyperoside).

The alcoholic mother liquor of hyperoside was diluted with water in stages, removing the sticky matter that separated at every stage. The final clear aqueous-alcoholic solution, on almost complete removal of the solvents and leaving in the ice-chest for three weeks, deposited a small quantity of a yellow solid embedded in a large amount of a syrupy matrix. Crystallization from aqueous acetone twice yielded yellow needles, m.p. 312–16° (0·3 g.) answering the description of quercetin. It further yielded an acetate, m.p. 196–98°, undepressed by admixture with an authentic sample of quercetin penta-acetate.

The aqueous residue of solution X remaining after ether extraction was hydrolysed by the addition of sulphuric acid to give a concentration of 7%

and refluxing for 2 hours. A large amount of resinous matter separated, which was filtered, washed, dried and extracted with ether. The ether-insoluble part of the resin was not examined further. The acidic filtrate was extracted with ether and this ether solution was united with the ether extract of the resinous portion. The united ether solution, on removal of the solvent, yielded quercetin (0·5 g.), m.p. 310–14°; acetate, m.p. 194–96° (mixed m.p. undepressed). The acid aqueous layer exhibited strong reducing property towards Fehling's solution indicating the rich presence of sugars.

Second extraction procedure

Only a very brief description of this procedure is given here. The powdered leaf was exhausted with ether and then with alcohol. The ether extract (solution) when shaken with aqueous alkali led to the separation of ursolic acid as the sparingly soluble sodium salt. The filtered alkaline solution yielded no crystalline substance. The ether solution was evaporated and the residue partitioned between 90% acetic acid and petroleum ether. The petroleum ether phase yielded epifriedelinol, m.p. 279–81°; $[\alpha]_D^{29} = +25{\cdot}6° \pm 3°$ ($c = 1{\cdot}156$ in chloroform). From the acetic acid phase, by dilution with water and ether extraction a small quantity of an amorphous material was obtained, which could not be further purified.

The alcoholic extract of the leaf gave colour reactions for anthoxanthins and on hydrolysis with sulphuric acid yielded, besides a large quantity of resinous material, a crystalline substance identified as quercetin.

Ursolic acid

When crystallized twice from alcohol, it separated as colourless needles, m.p. 280–82°; $[\alpha]_D^{30} = +62{\cdot}4° \pm 3°$ ($c = 1{\cdot}027$ in absolute alcohol). [Found: C, 78·6; H, 10·1. $C_{30}H_{48}O_3$ (ursolic acid) requires: C, 78·9; H, 10·6%.] With concentrated sulphuric acid it gave a yellow colour slowly changing to violet, and in the Liebermann-Burchard test it gave a red colour changing to violet, then blue and finally green.

The acetate, prepared by heating the substance with acetic anhydride and fused sodium acetate at 140° for 4 hours crystallized from benzene-petroleum ether and then from alcohol as colourless needeles, m.p. 282–84°; $[\alpha]_D^2 = +68{\cdot}8° \pm 3°$ ($c = 0{\cdot}927$ in chloroform). [Found: C, 76·7; H, 10·6; $-COCH_3$, 9·3. $C_{32}H_{50}O_4$ (ursolic acid acetate) requires; C, 77·1; H, 10·1; $-COCH_3$ (1), 8·6%.] Mixed m.p. with an authentic sample of ursolic acid acetate was undepressed.

Epifriedelinol

When crystallized twice from chloroform, it separated as stout needles, m.p. 280–81°; $[\alpha]_D^{29} = +22{\cdot}4° \pm 3°$ ($c = 0{\cdot}996$ in chloroform). [Found;

C, 84·7; H, 12·5. $C_{30}H_{52}O$ (epifriedelinol) requires: C, 84·1; H, 12·2%.] With concentrated sulphuric acid it gave a pale yellow colour. In the Liebermann-Burchard test a light pink colour was obtained.

Derivatives of epifriedelinol

(*a*) *Acetate.*—It was prepared by heating the substance with acetic anhydride and pyridine in a paraffin bath at 120° for 6 hours and purified by chromatography over alumina. The acetate crystallized from benzene-acetone as colourless plates, m.p. 282–84°; $[\alpha]_D^{30} = +30{\cdot}2° \pm 2°$ ($c = 0{\cdot}685$ in chloroform). [Found: C, 82·3; H, 11·8. $C_{32}H_{54}O_2$ (epifriedelinol acetate) requires: C, 81·6; H, 11·6%.]

(*b*) *Benzoate.*—The substance (0·15 g.) was dissolved in hot absolute pyridine (5 ml.), freshly distilled benzoyl chloride (1·0 ml.) was added and the mixture heated on a paraffin bath at 115° for 3 hours. It was cooled, diluted with a mixture of chloroform and ether (1 : 3) (50 ml.), transferred to a separating funnel and washed successively with 2 N sulphuric acid (3 × 10 ml.), 2 N sodium carbonate (3 × 10 ml.) and finally with water till neutral. The solution was dried, the solvents were removed and the residue was repeatedly crystallized from benzene-alcohol, when colourless plates, m.p. 248–50° were obtained. $[\alpha]_D^{30} = +36{\cdot}8° \pm 3°$ ($c = 0{\cdot}942$ in chloroform). [Found: C, 83·3; H, 11·1. $C_{37}H_{56}O_2$ (epifriedelinol benzoate) requires: C, 83·4; H, 10·6%.]

Hyperoside

When crystallized twice from water and twice from absolute alcohol, it separated as fine yellow needles, m.p. 238–40°; $[\alpha]_D^{29} = -65{\cdot}8° \pm 2°$ ($c = 0{\cdot}821$ in pyridine : alcohol 1 : 1). [Found on sample dried under vacuum at 110° for 10 hours and weighed in a closed pig: C, 53·2; H, 4·8. $C_{21}H_{20}O_{12}$ (hyperoside) requires C, 54·3; H, 4·3%.] It gave an orange-red colour with magnesium and hydrochloric acid and an olive-green colour with alcoholic ferric chloride. With neutral lead acetate solution a bright yellow precipitate was obtained. Molisch's test was positive.

Derivatives of hyperoside

(*a*) *Acetate.*—This was prepared by heating the substance with acetic anhydride and sodium acetate. It could not be crystallized from any solvent or solvent mixtures. By dissolving in benzene (charcoal) and adding excess of petroleum ether, it could be obtained as a micro-crystalline powder, m.p. 102–04°. [Found: C, 55·3; H, 4·9; —$COCH_3$, 44·0. $C_{37}H_{36}O_{20}$ requires: C, 55·5; H, 4·5; —$COCH_3$ (8), 43·0%.]

(*b*) ***Methyl ether***.—This was prepared by repeated traetment of the glycoside in methanol solution with diazomethane in ether. The product was crystallized from methanol, when almost colourless needles separated, m.p. 224–26°. [Found on sample dried under vacuum at 110° for 10 hours and weighed in a closed pig: C, 56·4; H, 5·9; —OCH_3, 23·0. $C_{25}H_{28}O_{12}$ (hyperoside tetramethyl ether) requires: C, 57·7; H, 5·4; —OCH_3 (4), 23·8%.] It gave no colour with ferric chloride.

The low carbon values for the glycoside and its methyl ether are perhaps due to traces of difficultly removable impurities. It may be mentioned in passing that Casparis *et al.*[10] also have reported for their sample of hyperoside carbon values about 1·1% lower than the theoretical.

Hydrolysis of hyperoside (*quantitative*)

The glycoside (weighed amount) was refluxed with N-sulphuric acid in 50% alcohol for 2 hours. The alcohol was removed under reduced pressure with occasional addition of small quantities of water. The resulting suspension was left in the ice-chest for a day. The precipitate that separated was filtered, washed with water, dried at 105° for 2 hours under vacuum and weighed. Aglycone obtained: 66·7%. Aglycone present in the glycoside as per calculations: 65·2%.

Hydrolysis of hyperoside (*preparative*)

The substance (0·3 g.) was refluxed with 7% sulphuric acid (100 ml.) in 50% alcohol for 2 hours. The solution was diluted with water, alcohol was removed and the aglycone that separated on standing was filtered and washed with water. Repeated crystallization from dilute alcohol (charcoal) gave fine yellow needles, m.p. 318–22°. [Found: C, 59·7; H, 3·8. $C_{15}H_{10}O_7$ (quercetin) requires: C, 59·6; H, 3·3%.] It gave a deep orange-red colour with magnesium and hydrochloric acid. With neutral lead acetate solution, an orange precipitate was obtained.

The acetate of this aglycone crystallized from alcohol as colourless needles, m.p. 197–98°. [Found: C, 59·4; H, 4·4. $C_{25}H_{20}O_{12}$ (quercetin penta-acetate) requires: C, 58·6; H, 3·9%.] Mixed m.p. with an authentic sample of quercetin penta-acetate was undepressed.

The acidic filtrate obtained after removing the aglycone was shaken with a little ether to remove the remaining aglycone and neutralized with excess of freshly precipitated barium carbonate. The suspension was filtered, washed with water and the filtrate and washings were united and concentrated to a syrupy residue under reduced pressure. The residue was

dissolved in a little water, filtered (charcoal) and the filtrate again reduced to a syrup.

The osazone prepared from a portion of the above sugar residue crystallized from dilute alcohol as characteristic yellow needles, m.p. 189–91° (decomp.). Mixed m.p. with an authentic sample of D-galactosazone was undepressed.

The identity of the sugar was further established by descending paper chromatography using butanol: acetic acid: water 4: 1: 5 (by volume) as the irrigating solvent and aniline hydrogen phthalate as the spray reagent.[16] Direct comparison of the sugar in question was made with pure D-glucose, pure D-galactose and L-pure rhamnose. Mixed chromatograms of the unknown with glucose and galactose separately were also run for further confirmation.

Hydrolysis of the methyl ether of the glycoside

The substance (50 mg.) was refluxed with 7% sulphuric acid in 50% alcohol (25 ml.) for 2 hours. The resulting solution was diluted with water to 50 ml. and extracted with ether (4×50 ml.). The ethereal extract was washed with water till neutral, dried and the solvent removed. On crystallizing the residue from alcohol (charcoal) light yellow needles, m.p. 194°, were obtained. [Found: C, 64·2; H, 5·5; —OCH_3, 33·4. $C_{19}H_{18}O_7$ (quercetin tetramethyl ether) requires: C, 63·7; H, 5·1; —OCH_3 (4), 34·6%.] Mixed m.p. with an authentic sample of 5: 7: 3′: 4′-O-tetramethylquercetin (m.p. 194°), kindly supplied by Prof. T. R. Seshadri of the Delhi University, was undepressed.

SUMMARY

The examination of the leaves of *Rhododendron nilagiricum* Zenk. by extraction with solvents is described. Ursolic acid, epifriedelinol and hyperoside have been isolated and characterized.

ACKNOWLEDGEMENTS

We are grateful to Prof. T. R. Seshadri of the Delhi University for the reference sample of tetramethylquercetin. We thank the Curator, Government Botanic Gardens, Ootacamund, for supplying the material used in this investigation and the Superintendent, Indian Botanic Garden, Calcutta, for confirming the botanical identity. We thank Mr. E. Venkata Rao for the microanalyses.

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THE STRUCTURE OF *ACACIA SUNDRA* GUM

Part II. The Structure of the Degraded Gum

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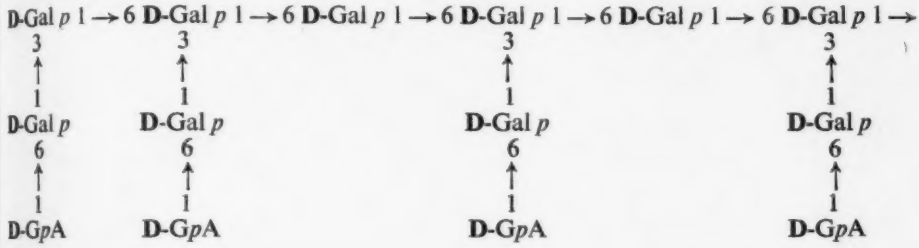
It was shown in Part I[1] that the *Acacia sundra* gum is composed of the following sugar residues, D-galactose, L-arabinose, L-rhamnose, D-glucuronic acid and a trace of another sugar probably xylose. Autohydrolysis of the gum removes L-rhamnose and most of L-arabinose residues with the formation of a degraded gum which is composed of D-galactose and D-glucuronic acid residues. Hydrolysis of the degraded gum with 0·1 N acid gave D-galactose, the aldobiouronic acid, 6-β-D-glucuronosyl-D-galactose and a small amount of L-arabinose which was probably present as an impurity.

This communication deals with the examination of the methylated sugars formed on hydrolysis of the methylated degraded gum. On the basis of the identification of these sugars and determination of their weights a tentative structure has been suggested for the degraded gum.

The degraded gum, prepared by autohydrolysis, was methylated first with dimethyl sulphate and then with silver oxide and methyl iodide. Methanolysis of the resulting methylated degraded gum yielded the methyl glycosides of methylated methyl glucuronate and galactose, which were separated as formerly described.[2] The acid component, 2, 3, 4-tri-*O*-methyl-**D**-glucuronic acid (4 mol. props.) was identified as methyl 2, 3, 4-tri-*O*-methyl-**D**-glucarate-1, 5-lactone whereas the neutral components after hydrolysis were shown by paper chromatography to consist of 2, 3, 4-tri-(6 mol. props.), 2, 4, 6-tri-(1 mol. prop.) and 2, 4-di-*O*-methyl-**D**-galactose (3 mol. props.), all three of which were transformed into their characteristic aniline derivatives.

Since the equivalent weight of the degraded gum was 570 (calculated from the barium content of the barium salt of the degraded gum) it is suggested, in agreement with the above results, that the average repeating unit of the gum consists of about 10 units of D-galactose and 4 units of D-glucuronic acid.

The isolation[1] of 6-β-D-glucuronosyl-D-galactose shows that the uronic acid units are joined to galactose by 1 → 6 bonds. Now if it be assumed that all of the aldobiouronic acid residues are linked in this manner and that they constitute side-chains, the formulation shown in I, which is analogous to that proposed[3] for degraded arabic acid, may be put forward as one of a number of possible structures for the average repeating unit of degraded *sundra* gum acid.



D-Gal *p* = D-Galactopyranose residue.
D-G*p*A = D-Glucopyranosyluronic acid residue.

Neither the distribution of the aldobiouronic acid side-chains along the main galactose chain nor the position of their attachment to this chain is known, but it is apparent that the galactose units at which branching occurs correspond to those which give rise to 2, 4-di-*O*-methyl-**D**-galactose and consequently they are linked through C_1, C_3 and C_6. The aldobiouronic acid side-chains may be attached either to C_3 as shown in (I), or to C_6, and it is also possible that both these structural features are present.

Of the remaining galactose units of the main chain it is evident that one is joined through C_3 and the other two through C_6; these postulations follow from the isolation of the 2, 4, 6-tri-*O*-methyl-**D**-galactose, and the remainder of the 2, 3, 4-tri-*O*-methyl-**D**-galactose not derived from the aldobiouronic acid side-chains. The presence of 1 → 3 linked D-galactose residues is supported by the previous observation[1] that the gum contains galactose units which survive periodate exidation.

Experimental

Unless otherwise stated, solutions were concentrated at 40–50° under reduced pressure; paper chromatographic separations were carried out by descending method on Whatman No. 1 paper using 1-butanol: ethanol: water (5: 1: 4, by volume—upper layer) as the irrigating solvent and *p*-anisidine phosphate[4] spray reagent was used to detect the sugars and uronic acids.

Isolation of barium salt of the degraded gum.—A solution of the purified gum (25 gm.) in water (500 ml.) was heated on a boiling water-bath for 80 hours. The hydrolysed solution was cooled and neutralised (barium hydroxide), filtered and evaporated to a thin syrup. It was then poured with stirring into methanol (500 ml.) and the precipitated material was washed with aqueous methanol and finally with methanol. It was dried in vacuum and the material so obtained was barium salt of the degraded gum (Ba 10·8%, yield 13 gm.). It reduced Fehling's solution.

Methylation of the degraded gum.—To a solution of barium salt of the degraded gum (13 gm.) in water (50 ml.) dimethyl sulphate (75 ml.) was added followed by sodium hydroxide (225 ml., 30%), added dropwise during 8 hours with stirring. After stirring for another 12 hours, the solution, which was non-reducing to Fehling's solution, was filtered and neutralised (sulphuric acid) when the partially methylated degraded gum precipitated out. It was again methylated by dissolving it in sodium hydroxide (200 ml., 30%) and adding dimethyl sulphate (105 ml.) as in the previous manner. The reaction mixture was acidified (sulphuric acid, acidic to congo red) when the methylated product precipitated out. It was dissolved in chloroform and filtered. The extract was methylated twice by the Purdie method[5] to give a yellowish brown solid (8·9) (OCH_3 42·4%). Its methoxyl content did not increase on further methylation.

Hydrolysis of the methylated degraded gum.—The methylated degraded gum (8·9 gm.) was dissolved in methanolic hydrogen chloride (180 ml.; 6·5%) and refluxed for 10 hours, cooled, neutralised (silver carbonate), filtered and the residue washed with methanol. The filtrate and washings were evaporated and the resulting syrup (9·2 gm.) was saponified with barium hydroxide (100 ml.; 0·3 N) at 55° for 2 hours. Excess of barium hydroxide in the solution was neutralised by passing carbon dioxide and the solution concentrated to a syrup. It was again saponified in the above manner, neutralised (carbon dioxide), filtered and the filtrate evaporated to dryness. Traces of moisture were removed by adding absolute alcohol repeatedly and distilling off the alcohol. The dried substance was extracted with ether. Fraction insoluble in ether was dissolved in water (150 ml.) and extracted with chloroform in a liquid-liquid extractor. Ether and chloroform extracts on evaporation gave a syrup (A) (5·8 gm.). The aqueous solution left after chloroform extraction was acidified (sulphuric acid, acidic to congo red) and again extracted with chloroform in a liquid-liquid extractor. The chloroform extract was evaporated to a syrup (B) (2·7 gm.).

Syrup (A) was hydrolysed (N hydrochloric acid, 100 ml.) by heating at 95–98° for 10 hours. The solution was neutralised (silver carbonate) and

filtered, and silver ions were removed from the filtrate by passage of hydrogen sulphide and filtration of precipitated silver sulphide. The filtrate was evaporated to a syrup (C) (5·7 gm.) and traces of moisture were removed from it by adding absolute alcohol repeatedly and distilling off the alcohol. Syrup (B) was hydrolysed (N hydrochloric acid, 75 ml.) in the same manner as described above and working up in the same way it yielded a syrup (D) (2·55 gm.).

Examination of syrup (*C*).—Syrup (C) which was a mixture of methylated sugars was examined on a paper chromatogram, when four spots were observed. The first one, very faint, red in colour and close to the origin, was due to a trace of uronic acid in the mixture. The second, third and fourth were yellow in colour and had R_G values 0·41, 0·62 and 0·68 respectively. These three fractions were separated on large sheets of filter-paper and the sugar-containing strips were eluted with water by Dent's method.[6] The eluted solutions were concentrated separately to give the following fractions:—

Fraction I.—(56·8 mgm.) R_G 0·41; OCH_3 29·1% calculated for di-*O*-methyl-**D**-galactose OCH_3 29·8%. Its aniline derivative was prepared in the usual way and recrystallised from alcohol, m.p. 207° reported m.p. of 2, 4-di-*O*-methyl-*N*-phenyl-**D**-galactosylamine is 204–16°.[7–9] A portion of the sugar was demethylated[10] with hydroiodic acid (48% w/w) and worked up in the usual way. On paper chromatographic examination the demethylated product gave a spot corresponding to **D**-galactose together with other spots of higher R_G values corresponding to methylated D-galactoses. The sugar was oxidised with periodic acid[11]; the oxidate on treatment with dimedone solution[11] gave the crystalline dimedone derivative of formaldehyde, m.p. and mixed m.p. 188°. It shows the presence of free hydroxyl group at C_6.

Fractions II.—(119·4 mgm.) R_G 0·62; OCH_3 40·9%, calculated for tri-*O*-methyl-**D**-galactose, 41·9%. Its aniline derivative was prepared in the usual way and recrystallised from alcohol, m.p. and mixed m.p. with 2, 3, 4-tri-*O*-methyl-*N*-phenyl-**D**-galactosylamine 166°. Paper chromatographic examination of demethylated sugar gave spots of D-galactose and partially demethylated derivatives of 2, 3, 4-tri-*O*-methyl-**D**-galactose.

Fraction III.—(17·4 mgm.) R_G 0·68. Its aniline derivative was prepared in the usual way and recrystallised from alcohol, m.p. and mixed m.p. with 2, 4, 6-tri-*O*-methyl-*N*-phenyl-**D**-galactosylamine 180°; OCH_3 32·2%, calculated for tri-*O*-methyl-*N*-phenyl-**D**-galactosylamine 31·3%. The aniline derivative was demethylated[10] and simultaneously hydrolysed with

hydroiodic acid (48% w/w) and worked up in the usual way. It gave spots of D-galactose and partially demethylated derivatives of 2, 4, 6-tri-*O*-methyl-D-galactose on a paper chromatogram.

Examination of syrup (*D*).—It was examined on paper chromatogram using 1-butanol : acetic acid : water (4 : 1 : 5, by volume—upper layer) as the irrigating solvent. It showed one main spot, R_G 0·82 (reported R_G 0·84 for 2, 3, 4-tri-*O*-methyl-D-glucuronic acid)[12] and traces of two slower moving components R_G 0·73 and 0·61 respectively which gave red spots on paper chromatogram. The syrup (D) (OCH_3 38·4%; calculated for tri-*O*-methyl hexuronic acid OCH_3 39·5%) was oxidised with bromine and identified as methyl 2, 3, 4-tri-*O*-methyl-D-glucuronate-1, 5-lactone, (α) D^{28} + 54° (after 24 hours in methanol, C. 1%), m.p. 106° by the method described in the previous paper.[1]

SUMMARY

The degraded gum forms the basic nucleus of the whole gum; during autohydrolysis the labile sugar residues which are attached glycosidically to the main structure are removed and the degraded gum is obtained. The degraded gum is reducing in nature and consists of a repeating unit of ten D-galactose residues and four D-glucuronic acid residues. Methylation and subsequent hydrolysis of the resulting methyl ester of the methylated degraded polysaccharide furnished 2, 3, 4-tri-(6 mol. props.); 2, 4, 6-tri-(1 mol. prop.) and 2, 4-di-*O*-methyl-D-galactose (3 mol. props.) and 2, 3, 4-tri-*O*-methyl-D-glucuronic acid (4 mol. props.). On the basis of the identification of the methylated derivatives and their respective molecular proportions a tentative structure has been suggested for the degraded gum.

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TEMPERATURE VARIATION OF THE ELASTIC CONSTANTS OF BARYTES

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1. Introduction

It has been recognised from a long time that studies on temperature variations of elastic constants of single crystals play an important part in our understanding of crystalline forces. A number of simple cubic crystals have been studied by employing ultrasonic methods of investigation (*see* Bergmann, 1954). But very little work has been done on non-cubic crystals. In this laboratory, we have addressed ourselves to a study of this problem. Barytes has been chosen as it was readily available. It crystallises in the orthorhombic system and belongs to the space group V_h^{16}. According to Voigt (1928) it has 9 independent elastic constants. Temperature variations of these constants in the range 35 to 185° C. have been reported here.

2. Experimental Technique

In this investigation, the composite piezo-electric oscillator method developed by Balamuth (1934) has been employed. Essentially the method is one of determining the natural frequency of a loaded bar executing either longitudinal or torsional oscillations. An X-cut quartz bar, approximately 2 cm. long and 0·3 cm. square cross-section, is taken. Such a bar vibrates in a longitudinal mode. It is excited by a precision oscillator capable of reading to $\pm$ 40 cycles per second. The natural frequency F_1 of the bar is determined using a vacuum-tube voltmeter as a detector of resonance. A bar of the specimen material of the same cross-section but of natural frequency F_2 very nearly equal to F_1 is taken and cemented to the quartz bar using a suitable adhesive. The natural frequency F_0 of the composite oscillator is measured. The fundamental frequency F_2 of the specimen bar is given by

$F_2 = F_0 + M_1 (F_0 - F_1)/M_2$ where M_1 and M_2 are the masses of the quartz and the specimen bars. The longitudinal elastic constant for

the specimen is given by $S_{33}' = 4\,L^2\,F_2^2\,\rho$ where L is the length of the specimen and ρ is its density.

For exciting torsional oscillations, a Y-cut quartz rod of about 2 cm. length and 0·4 cm. diameter with electrode arrangements suggested by Giebe and Scheibe (1928) is used. The natural frequency of the specimen rod determined in the same manner now gives its torsional elastic constant through the relation

$$2\,(S_{44}' + S_{55}') = 4\,L^2\,F_2^2\,\rho.$$

In the case of crystalline materials S_{33}' is the effective value of the longitudinal elastic constant for a crystal bar with its length along Z′ whose direction-cosines are α_{13}, α_{23} and α_{33} with the crystallographic axes X, Y and Z respectively (*see* Wooster, 1938). Similarly, $2\,(S_{44}' + S_{55}')$ is the torsion constant for a cylindrical rod with its axis along Z′.

A suitable number of such determinations have to be made to find all the elastic constants of a crystal. For barytes, 6 rectangular bars and 3 cylindrical rods of suitable orientations are required. The orientations of these bars and rods are described in Table I.

TABLE I

Description of orientations of crystal bars and rods of barytes

Sl. No.	Name of the bar or rod	Direction cosines			Longitudinal constant S_{33}'	Torsional constant $2\,(S_{44}' + S_{55}')$
		α_{13}	α_{23}	α_{33}		
1	X	1	0	0	S_{11}	$2\,(S_{55} + S_{66})$
2	Y	0	1	0	S_{22}	$2\,(S_{66} + S_{44})$
3	Z	0	0	1	S_{33}	$2\,(S_{44} + S_{55})$
4	X 45° Z	$\sqrt{\frac{1}{2}}$	0	$\sqrt{\frac{1}{2}}$	$\frac{1}{4}\,[(S_{11} + S_{33}) + (4S_{55} + 2S_{31})]$	..
5	X 45° Y	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	0	$\frac{1}{4}\,[(S_{11} + S_{22}) + (4S_{66} + 2S_{12})]$	..
6	Y 45° Z	0	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	$\frac{1}{4}\,[(S_{22} + S_{33}) + (4S_{44} + 2S_{23})]$	..

The first three bars and rods give the diagonal terms of the elasticity tensor; the next three give the non-diagonal terms. In the case of bar 4, X 45° Z means that its length makes angles of 45° with respect to X and Z and is perpendicular to Y. Similar meanings are attached to bars 5 and 6.

The composite oscillator is placed in an electrical furnace whose temperature could be raised up to 200° C. and controlled to $\pm 1°$ C. at any desired point. The resonant frequency of the composite bar is determined at each temperature. The data thus obtained are used to evaluate the manner in which the effective elastic constants of the bars and rods vary with temperature.

3. EXPERIMENTAL RESULTS

Clear and transparent specimens of barytes $3'' \times 3'' \times 2''$ were used in this investigation. In these crystals the cleavage planes (001) showed out very clearly and the crystallographic Z-axis was taken perpendicular to this plane. Directions of X and Y axes were marked out by using polarised light. A contact goniometer was used to lay out the directions of cut described in Table I.

The masses of the quartzs and the specimens were determined with a Bunge balance to an accuracy of $\pm 0{\cdot}2$ mgm. The density of the specimen was found by the hydrostatic bench method to an accuracy of 1 in 1,000 or better. It is known that the density of barytes does not change with temperature (*International Critical Tables*, 1933) and therefore the room temperature value was used in all calculations. Length of each bar or rod was measured with a precision microscope to an accuracy of 0·01 mm. in a length of approximately 2 cm. Temperature variations of length were calculated by using the data of Sarma (1951).

Results obtained at room temperature have been given in Table II and compared with those of the previous workers.

TABLE II

Elastic constants of barytes (*Density* = 4·517 *gm./c.c.*)

	S_{11}	S_{22}	S_{33}	S_{44}	S_{55}	S_{66}	S_{12}	S_{13}	S_{23}
Voigt ..	16·4	18·9	10·6	84·0	34·8	36·0	−9·0	−1·9	−2·5
Bergmann	17·2	19·9	10·9	85·5	35·8	39·2	−9·9	−1·7	−3·0
Seshagiri Rao	18·40	17·36	10·96	83·33	34·84	36·50	−9·45	−2·68	−2·73
Authors ..	16·57	19·06	10·67	82·12	36·82	36·98	−8·65	−3·62	−1·73

S's are expressed in the units of 10^{-12} cm.²/dyne.

It will be seen from Table I that in this method, the constants S_{11}, S_{22} and S_{33} are determined directly. The constants S_{44}, S_{55} and S_{66} are determined by solving simple combinations as in the case of Voigt's work. Therefore agreement with Voigt's values is very good in these cases. The non-diagonal terms are obtained from more complicated equations and hence there is a chance of differences showing out in an exaggerated manner. This explains the large differences in the values for S_{13} and S_{23}.

Temperature variations of S_{11}, S_{22} and S_{33} are obtained from measurements on X, Y and Z bars. It is found that they increase linearly with temperature. Temperature variations of torsion constants for the X, Y and Z rods are shown in Fig. 1. The torsion constants $2(S_{55} + S_{66})$ and

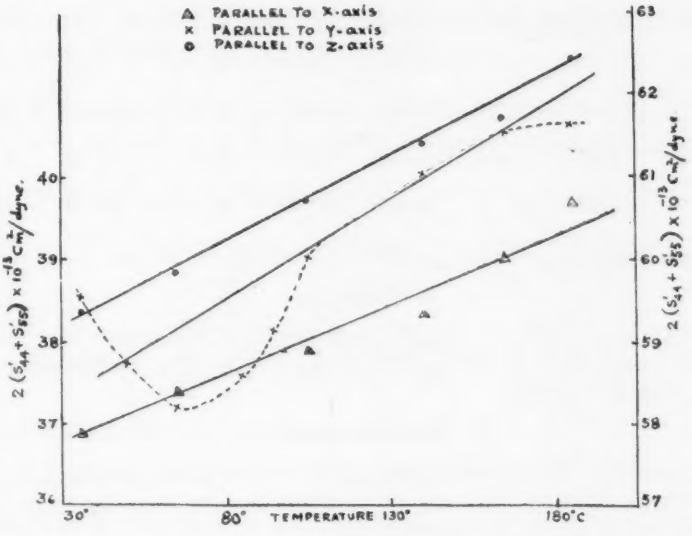

FIG. 1

$2(S_{44} + S_{55})$ for the X and Z rods also show a linear increase in their values with rise of temperature. But the torsion constant $2(S_{66} + S_{44})$ for the Y-rod decreases with temperature reaching a minimum in the neighbourhood of 65° C. and then increases with further rise in temperature. The range of this variation is several times the allowable margin of errors and so the effect is very definite. The longitudinal constants of bars, X 45° Y and X 45° Z show the normal rise with temperature. The longitudinal constants for the bar Y 45° Z decreases with temperature till 140° C. and then remains

unchanged over a considerable range till 165° C. is reached; after which it once again falls down with further rise of temperature.

From these sets of observations, temperature variations of individual elastic constants are calculated and presented in Table III.

TABLE III

Temperature variation of elastic constants of barytes

Temperature °C.	S_{11}	S_{22}	S_{33}	S_{44}	S_{55}	S_{66}	S_{23}	S_{31}	S_{12}
35	16·57	19·06	10·67	82·12	36·82	36·98	− 1·73	− 3·62	− 8·65
65	16·82	19·25	10·76	80·63	39·03	35·79	− 3·01	− 4·33	− 7·23
105	17·02	19·36	10·87	82·88	38·68	37·10	− 7·03	− 2·09	− 7·96
140	17·23	19·47	10·95	84·07	38·61	38·01	− 11·05	− 0·83	− 8·67
165	17·45	19·61	11·04	84·09	39·15	38·91	− 10·86	− 0·08	− 9·65
185	17·50	19·83	11·11	84·19	40·61	38·95	− 12·33	− 0·26	− 9·36

S's are in the units of 10^{-13} cm.²/dyne.

4. SUMMARY

Temperature variation of the elastic constants of barytes has been studied in the temperature range 35 to 185° C. employing the composite piezo-electric oscillator method.

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SOME GENERAL KERNELS FOR THE DERIVATION OF SELF-RECIPROCAL FUNCTIONS

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Introduction

The aim of this paper is to give some new kernels and deduce some self-reciprocal functions under the Hankel transform.

2. A function $f(x)$ is said to be self-reciprocal under Hankel's transform and is denoted by R_ν if the following integral equation is satisfied:

$$f(y) = \int_0^\infty f(x)\sqrt{xy}\,J_\nu(xy)\,dx \tag{2.1}$$

where $J_\nu(x)$ is the Bessel function of order ν. Titchmarsh[1] gives that $f(x)$ is R_ν if

$$f(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} 2^{S/2}\,\Gamma\left(\frac{S}{2}+\frac{\nu}{2}+\frac{1}{4}\right)\psi(S)\,x^{-S}\,dS\ 0 < c < 1 \tag{2.2}$$

where $\psi(S)$ satisfies the functional relation

$$\psi(S) = \psi(1-S). \tag{2.3}$$

In other words $f(x)$ R_ν is if its Mellin transform is of the form

$$2^{S/2}\,\Gamma\left(\frac{S}{2}+\frac{\nu}{2}+\frac{1}{4}\right)\psi(S)$$

where $\psi(S)$ satisfies (2.3)

Again if $f(x)$ is R_μ and

$$g(x) = \int_0^\infty f(y)\,h(xy)\,dy \tag{2.4}$$

is R_ν then $h(x)$ is called a kernel which carries R_μ into R_ν.

Titchmarsh[1] gives that if

$$h(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^s \Gamma\left(\frac{s}{2} + \frac{\nu}{2} + \frac{1}{4}\right) \Gamma\left(\frac{s}{2} + \frac{\mu}{2} + \frac{1}{4}\right) \phi(s)\, x^{-s}\, ds$$

$$0 < c < 1 \qquad (2.5)$$

where

$$\phi(s) = \phi(1 - s) \qquad (2.6)$$

then $h(x)$ is a kernel which carries R_μ into R_ν. The symmetry of (2.5) in μ and ν suggests that $h(x)$ transforms R_ν into R_μ also. In other words if the Mellin transform of $h(x)$ is

$$2^s \Gamma\left(\frac{s}{2} + \frac{\mu}{2} + \frac{1}{4}\right) \Gamma\left(\frac{s}{2} + \frac{\nu}{2} + \frac{1}{4}\right) \phi(s)$$

where $\phi(s)$ satisfies (2.6), then $h(x)$ is a kernel which carries R_μ into R_ν and *vice versa*.

3. It is now proposed to prove that

$$x^{1/2} K_{\mu/2-\nu/2}(\alpha x)\, J_{\mu/2+\nu/2}(\beta x)$$

is a kernel which carries R_μ into R_ν provided $\alpha^2 + \beta^2 = 1$.

Watson[2] gives that

$$\int_0^\infty K_\mu(\alpha t)\, J_\nu(\beta t)\, t^{-\rho}\, dt = \frac{\beta^\nu \Gamma\left(\frac{\nu-\rho+\mu+1}{2}\right) \Gamma\left(\frac{\nu-\rho-\mu+1}{2}\right)}{2^{\rho+1}\, \alpha^{\nu-\rho+1}\, \Gamma(\nu+1)}$$

$$\times {}_2F_1\left(\frac{\nu-\rho+\mu+1}{2}, \frac{\nu-\rho-\mu+1}{2}; \nu+1; -\frac{\beta^2}{\alpha^2}\right).$$

$$Re(\alpha \pm i\beta) > 0 \qquad Re(\nu - \rho + 1 \pm \mu) > 0 \qquad (3.1)$$

Taking $-\rho = \lambda - 1$, we have that

$$\int_0^\infty K_\mu(\alpha t)\, J_\nu(\beta t)\, t^{\lambda-1}\, dt = \frac{\beta^\nu \Gamma\left(\frac{\nu+\mu+\lambda}{2}\right) \Gamma\left(\frac{\nu-\mu+\lambda}{2}\right)}{2^{2-\lambda}\, \alpha^{\nu+\lambda}\, \Gamma(\nu+1)}$$

$$\times {}_2F_1\left(\frac{\nu+\mu+\lambda}{2}, \frac{\nu-\mu+\lambda}{2}; \nu+1; -\frac{\beta^2}{\alpha^2}\right)$$

$$Re(\alpha \pm i\beta) > 0, \qquad Re(\nu + \lambda \pm r) > 0 \qquad (3.2)$$

By writing the Hypergeometric series $F(a, b; c; z)$ as

$$(1-z)^{-a} F\left(a, c-b; c; \frac{z}{z-1}\right)$$

assuming that $|z| < \frac{1}{2}$ we have from (3.2) that

$$\int_0^\infty K_\mu(\alpha t) J_\nu(\beta t) t^{\lambda-1} dt$$

$$= \frac{\beta^\nu \Gamma\left(\frac{\nu+\mu+\lambda}{2}\right) \Gamma\left(\frac{\nu-\mu+\lambda}{2}\right)}{2^{2-\lambda} \alpha^{\nu+\lambda} \Gamma(\nu+1)} \left(\frac{\alpha^2}{\alpha^2+\beta^2}\right)^{(\nu+\mu+\lambda)/2}$$

$$\times {}_2F_1\left(\frac{\nu+\mu+\lambda}{2}, \frac{\nu-\mu+\lambda}{2}; \nu+1; \frac{\beta^2}{\alpha^2+\beta^2}\right). \quad (3.3)$$

From (3.3), we get that the Mellin transform of

$$x^{1/2} K_\mu(\alpha x) J_\nu \beta x)$$

is

$$C\, 2^\lambda \Gamma\left(\frac{\lambda}{2}+\frac{\nu}{2}+\frac{\mu}{2}+\frac{1}{4}\right) \Gamma\left(\frac{\lambda}{2}+\frac{\nu}{2}-\frac{\mu}{2}+\frac{1}{4}\right)$$

$$\times {}_2F_1\left(\frac{\nu}{2}+\frac{\mu}{2}+\frac{\lambda}{2}+\frac{1}{4}, \frac{\nu}{2}+\frac{\mu}{2}-\frac{\lambda}{2}+\frac{3}{4}; \nu+1; \beta^2\right) \quad (3.4)$$

provided $\alpha^2 + \beta^2 = 1$ where C is a constant not involving λ which satisfies conditions laid down in § 2.

Hence

$$x^{1/2} K_\mu(\alpha x) J_\nu(\beta x)$$

is a kernel which carries $R_{\nu-\mu}$ into $R_{\nu+\mu}$ and *vice versa* provided $\alpha^2 + \beta^2 = 1$.

Taking $\nu + \mu = \nu$, $\nu - \mu = \nu$ we have that

$$x^{1/2} K_{(\mu-\nu)/2}(\alpha x) J_{(\mu+\nu)/2}(\beta x)$$

is a kernel which carries R_μ into R_ν and *vice versa* provided $\alpha^2 + \beta^2 = 1$ and $Re\ (\mu, \nu) > -1$.

We now give the particular cases. If $\beta \to 0$ then $\alpha \to 1$ and we get that

$$x^{(\mu+\nu+1)/2} K_{(\mu-\nu)/2}(x)$$

is a kernel which carries R_μ into R_ν and *vice versa* as given by Titchmarsh.[1]

Taking

$$a = \beta = \frac{1}{\sqrt{2}}, \quad \nu = 0$$

we have that

$$x^{1/2} J_\mu\left(\frac{x}{\sqrt{2}}\right) K_\mu\left(\frac{x}{\sqrt{2}}\right)$$

is a kernel which carries R_0 into R_μ and *vice versa* as given by Gupta.[3]

4. Similarly we prove that

$$x^{1/2} J_{(\mu+\nu)/2}(\alpha x) J_{(\mu-\nu)/2}(\beta x)$$

is a kernel which carries R_μ into R_ν and *vice versa* provided $\alpha^2 - \beta^2 = 1$. Watson[2] gives that

$$\int_0^\infty J_\mu(at) J_\nu(\beta t) t^{-\rho} dt$$

$$= \frac{a^\mu \Gamma\left(\frac{\nu+\mu-\rho+1}{2}\right)}{2^\rho \beta^{\mu-\rho+1} \Gamma(\mu+1) \Gamma\left(1+\frac{\nu}{2}-\frac{\rho}{2}-\frac{\mu}{2}\right)}$$

$$\times {}_2F_1\left(\frac{\nu+\mu-\rho+1}{2}, \frac{\mu-\nu-\rho+1}{2}, \mu+1; \frac{a^2}{\beta^2}\right)$$

$$Re(\nu+\mu-\rho+1) > 0, \qquad Re\,\rho > -1, \qquad 0 < a < \beta. \tag{4.1}$$

(4.1) can be rewritten as

$$\int_0^\infty J_\mu(at) J_\nu(\beta t) t^{\lambda-1} dt$$

$$= \frac{a^\mu \Gamma\left(\frac{\nu+\mu+\lambda}{2}\right)}{2^{1-\lambda} \Gamma(\mu+1) \Gamma\left(1+\frac{\nu-\mu-\lambda}{2}\right) \beta^{\mu+\lambda}}$$

$$\times {}_2F_1\left(\frac{\nu+\mu+\lambda}{2}, \frac{\mu-\nu+\lambda}{2}; \mu+1; \frac{a^2}{\beta^2}\right)$$

$$Re(\nu+\mu+\lambda) > 0 \quad \text{and} \quad \lambda > 2 \tag{4.2}$$

proceeding similarly to § 3 we get that the Mellin transform of

$$x^{1/2} J_{(\mu+\nu)/2}(\alpha x) J_{(\mu-\nu)/2}(\beta x)$$

$$\frac{C2^S\Gamma\left(\frac{S}{2}+\frac{\mu}{2}+\frac{1}{4}\right)\Gamma\left(\frac{S}{2}+\frac{\nu}{2}+\frac{1}{4}\right)\times {}_2F_1\left(\frac{\mu}{2}+\frac{S}{2}+\frac{1}{4},\ \frac{\mu}{2}-\frac{S}{2}+\frac{3}{4};\ \frac{\mu}{2}+\frac{\nu}{2}+1;\ \alpha^2\right)}{\Gamma\left(\frac{\nu}{2}+\frac{S}{2_1}+\frac{1}{4}\right)\Gamma\left(\frac{\nu}{2}-\frac{S}{2}+\frac{3}{4}\right)} \tag{4.3}$$

provided $\alpha^2 - \beta^2 = 1$ and $|\alpha^2/\beta^2| < \frac{1}{2}$ where C is a constant not involving S.

Hence we get that

$$x^{1/2}\, J_{(\mu+\nu)/2}(\alpha x)\, J_{(\mu-\nu)/2}(\beta x)$$

is kernel which carries R_μ into R_ν and *vice versa* provided $\alpha^2 - \beta^2 = 1$ and $Re\,(\mu, \nu) > -1$.

Particular case: Making $\beta \to 0$ we get that

$$x^{(\mu-\nu+1)/2}\, J_{(\mu+\nu)/2}(x)$$

is a kernel which carries R_μ into R_ν and *vice versa* given by Titchmarsh.[1]

5. In § 3 we have proved that

$$x^{1/2}\, K_{(\mu-\nu)/2}(\alpha x)\, J_{(\mu+\nu)/2}(\beta x)$$

is a kernel which carries R_μ into R_ν and *vice versa* provided $\alpha^2 + \beta^2 = 1$. Taking $\beta = i\beta$ and using the relation

$$J_\mu(ix) = i^\mu I_\mu(x)$$

we get that

$$x^{1/2}\, i^{(\mu+\nu)/2}\, K_{(\mu-\nu)/2}(\alpha x)\, I_{(\mu+\nu)/2}(\beta x)$$

is a kernel which carries R_μ into R_ν provided $\alpha^2 - \beta^2 = 1$. Leaving the constant factor we get that

$$K_{(\mu-\nu)/2}(\alpha x)\, I_{(\mu+\nu)/2}(\beta x)\, x^{1/2}$$

is a kernel which carries R_μ into R_ν and *vice versa* provided $\alpha^2 - \beta^2 = 1$ and $Re\ (\mu, \nu) > -1$.

Particular case: Making $\beta \to 0$ we get the well known result that

$$x^{(\mu+\nu+1)/2}\, K_{(\mu+\nu)/2}(x)$$

is a kernel which carries R_μ into R_ν.

6. We now use the kernels given above on some of the known self-reciprocal functions and deduce new self-reciprocal functions. $x^{1/2} e^{-x^2/2}$ is R_0 and from § 4 we have that

$$t^{1/2} J_\mu(\alpha t) J_\mu(\beta t)$$

is a kernel which carries R_0 into $R_{2\mu}$ provided $\alpha^2 - \beta^2 = 1$. Hence

$$g(x) = \int_0^\infty t^{1/2} e^{-t^2/2} (xt)^{1/2} J_\mu(\alpha x t) J_\mu(\beta x t)\, dt \tag{6.1}$$

is $R_{2\mu}$. By 13.31 Watson we have that

$$y^{1/2} \exp.\left\{-\frac{1+2\alpha^2}{2} y^2\right\} I_\mu\{\alpha\sqrt{1+\alpha^2}\, y^2\} \text{ is } R_{2\mu}. \tag{6.2}$$

If $\alpha \to 0$ we get that $x^{2\mu+1/2} e^{-x^2/2}$ is $R_{2\mu}$.

We know that

$$x^{1/2} J_{(\mu+\nu)/2}(\alpha x) J_{(\mu-\nu)/2}(\beta x)$$

is a kernel which carries R_μ into R_ν provided $\alpha^2 - \beta^2 = 1$. Erdelyie and others[4] give that

$$\int_0^\infty J_\mu(\alpha t) J_\nu(\beta t) e^{-\lambda^2 t^2} t^{S-1}\, dt$$

$$= \frac{\alpha^\mu \beta^\nu}{2^{\mu+\nu} \lambda^{\mu+\nu+S} \Gamma(\nu+1)} \sum_{m=0}^\infty \frac{\Gamma(S+\mu+\nu+2m)}{m!\,\Gamma(\mu+m+1)} \left(\frac{-\alpha}{4\lambda^2}\right)^m$$

$$\times {}_2F_1\left(-m, -\mu-m; \nu+1; \frac{\beta^2}{\alpha^2}\right) \tag{6.3}$$

$Re\,(S+\mu+\nu) > 0.$

By making suitable adjustments we get that

$$\int_0^\infty (xt)^{1/2} J_{\mu(+\nu)/2}(\alpha x t) J_{(\mu-\nu)/2}(\beta x t) e^{-t^2/2} t^{\nu+1/2}\, dt$$

$$= x^{\mu+1/2} \sum_{m=0}^\infty \frac{\Gamma(\mu+\nu+2m+2)}{m!\,\Gamma\left(\frac{\mu+2m+2}{2}\right)} \left(\frac{-\alpha^2 x^2}{2}\right)^m$$

$$\times {}_2F_1\left(-m, \frac{-\mu}{2} - m; \frac{\nu}{2}+1; \frac{\beta^2}{\alpha^2}\right). \tag{6.4}$$

(6.4) gives an R_μ function provided $\alpha^2 - \beta^2 = 1$. When $\beta^2 = 0$ we get from (6.4) $x^{\mu+1/2} e^{-x^2/2}$ as a particular case.

Using the above kernel on

$$x^{\nu+2n+1/2} e^{-x^2/2} L_n^{n+\nu}\left(\frac{x^2}{2}\right)$$

which is R_ν for integral values of n we get on using the integral (6.3) after simplification that

$$y^{\mu+1/2} \sum_{m=0}^{n} \sum_{K=0}^{\infty} \frac{(-1)^m 2^{m/2} \Gamma\left(\frac{2K+2n+3\mu+m-\nu+2}{2}\right)}{m!\, K!\, \Gamma\left(\frac{2K+\mu-\nu+2}{2}\right)}$$

$$\left(-\frac{a^2x^2}{2}\right)^K {}_2F_1\left(-K, -\frac{2K+\mu+\nu}{2}; \frac{\mu-\nu+2}{2}; \frac{\beta^2}{a^2}\right) \quad (6.5)$$

is R_μ provided $a^2 - \beta^2 = 1$.

7. Erdelyie and others[5] give that the Mellin transform of $e^{-ax} J_\mu(\beta x)$ is

$$\frac{\beta^\nu \Gamma(S+\nu)}{2^\nu a^{\nu+S} \Gamma(\nu+1)} {}_2F_1\left(\frac{S+\nu}{2}, \frac{S+\nu+1}{2}; \nu+1; -\frac{\beta^2}{a^2}\right)$$

$$Re\, a > |Im\, \beta|\ Re\, S > -Re\, \nu. \quad (7.1)$$

By effecting suitable changes we have that

$$t^{1/2} e^{-at^2} J_{\nu/2}(\beta t^2)$$

has

$$C \cdot 2^{S/2} \Gamma\left(\frac{\nu}{2} + \frac{S}{2} + \frac{1}{4}\right) \times {}_2F_1\left(\frac{S}{4} + \frac{\nu}{2} + \frac{1}{8}, \frac{\nu}{2} - \frac{S}{4} + \frac{3}{8}; \right.$$

$$\left. \frac{\nu}{2} + 1; \frac{\beta^2}{a^2\beta^2}\right)$$

as its Mellin transform provided $a^2 + \beta^2 = 1$ where C is a constant. Hence by § 3 we have that $t^{1/2} e^{-at^2} J_{\nu/2}(\beta t^2)$ is R_ν provided $a^2 + \beta^2 = \frac{1}{4}$. Making $\beta \to 0$ we get that $t^{\nu+1/2} e^{-t^2/2}$ is R_ν which is a well-known result (7.2).

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PHOTO-PRODUCTION OF PION PAIRS BY POLARISED NUCLEONS

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Abstract

The problems of production of pion pairs by polarised photon beams on polarised nucleons is examined. It is found that the angular distribution of pion pairs is sensitive to the state of polarisation of the incident photon beam.

1. Introduction

Since the detection of longitudinal polarisation of beta particles (*see*, for example, Lee and Yang, 1956 and Wu *et al.*, 1957) polarisation phenomena has become quite an important criterion in all quantum mechanical processes. Besides its own intrinsic value, this has become a test for any particular theory of interaction. For example, we may consider the static theory of pion nucleon interaction which has been checked qualitatively and to a small extent quantitatively. Since most of the recent calculations are based on the static theory, it has become necessary to subject the static theory to a severe test within the range of its applicability. The photo mesons from polarised nucleons can be expected to be sensitive to the state of polarisation of the nucleon as well as the incident photon. In a recent contribution in these *Proceedings*, we have obtained some distinctive features of the angular distribution of photo mesons resulting from an incident beam of three to four hundred MEV. These calculations are done on the assumption that production of two or more mesons is negligible. If we wish to consider incident

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photon energies of about six or seven hundred MEV., it is necessary to take into account double production of mesons. In this paper, we shall obtain angular distribution of photo-pion pairs using a polarised beam of photons on a polarised nucleon.

2. Angular Distribution of $(\pi^+ \pi^-)$ Pairs Produced by Polarized Photons

The general method of arriving at the amplitude for production of photo-pion pairs by a nucleon has been discussed by us in an earlier contribution (Srinivasan and Venkatesan, 1959). The relevant amplitude is given by

$$F(\pi^+ \pi^-) = \frac{(4\pi)^{3/2}}{(8\omega_1\omega_2 k)^{1/2}} GH \tag{1}$$

where

$$G = \frac{f\sqrt{2}\sigma \cdot q_1 \tau_+}{\omega_1} \tag{2}$$

$$H = \frac{(\mu_p - \mu_n)\, e}{4mf} \left\{ \frac{1}{\sqrt{2}} (\tau_- \tau_3 + \tau_3 \tau_-) - \frac{\sqrt{2}}{3} \tau_- \tau_3 \right\}$$

$$\times \{2q_2 \cdot (k \times \lambda) - i\sigma \cdot (q_2 \times [k \times \lambda])\} \frac{a_{32}}{q_2^2} + \frac{ief}{\sqrt{2}}$$

$$\times (\tau_- \tau_3 - \tau_3 \tau_-) \left\{ \sigma \cdot \lambda + \frac{2\sigma \cdot (k - q_2)(q_2 \cdot \lambda)}{(k - q_2)^2 + 1} \right\}. \tag{3}$$

Note that G and H are matrices in the spin and isotopic spin space of the nucleon. For the sake of convenience, we denote

$$\frac{1}{q_2} \left(e^{i\delta_{33}(q_2)} \sin \delta_{33}(q_2) \right)$$

by a_{32}. The other symbols represent the same quantities as in the previous paper.

Let us choose a co-ordinate system with Z-axis in the direction of the photon propagation. In this system, the spherical polar angles of q_2 and q_1 are (θ_2, ϕ_2) and (θ_1, ϕ_1) respectively. We assume throughout this paper that the initial spin direction of the nucleon is along the direction of propagation of the photon. We make the same approximation as in a previous paper on single photo-production of mesons from polarised nucleons (*see* reference 2), *i.e.*, we neglect the pion current term for reasons mentioned there. The cross-sections for right and left circularly polarised photons for the

cases when either (i) there is a spin-flip, or (ii) there is no spin-flip for the nucleon are then given by the following expressions:

$$\frac{d^3\sigma_{\text{r.c.}}^{(1)}}{d\Omega_+ d\Omega_- d\omega_1} = \frac{e^2(\mu_p - \mu_n)^2 k q_1^3 \cos^2\theta_1 \sin^2\theta_2 \; a_{32}^2}{32\pi^2 m^2 \omega_1^2 q_2} \tag{4}$$

$$\frac{d^3\sigma_{\text{r.c.}}^{(2)}}{d\Omega_+ d\Omega_- d\omega_1} = \frac{e^2(\mu_p - \mu_n)^2 k q_1^3 \sin^2\theta_1 \; \sin^2\theta_2 \; a_{32}^2}{64\pi^2 m^2 \omega_1^2 q_2} \tag{5}$$

$$\begin{aligned}\frac{d^3\sigma_{\text{l.c.}}^{(1)}}{d\Omega_+ d\Omega_- d\omega_1} = \frac{2e^2 q_1 q_2}{\pi^2 \omega_1^2} \Bigg\{ & \left(\frac{(\mu_p - \mu_n)}{24m}\right)^2 \frac{k q_1^2 |a_{32}|^2 \cos^2\theta_1 \sin^2\theta_2}{q_2^2} \\ & + \frac{f^4 q_1^2}{4k} \left| 1 - \frac{(\mu_p - \mu_n) k a_{32} \cos\theta_2}{12 m f^2 q_2} \right|^2 \sin^2\theta_1 \\ & - \frac{(\mu_p - \mu_n) f^2 q_1^2 |a_{32}|}{48 m q_2} \left| 1 - \frac{(\mu_p - \mu_n) k a_{32} \cos\theta_2}{12 m f^2 q_2} \right| \\ & \times \sin 2\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \Bigg\}\end{aligned} \tag{6}$$

$$\begin{aligned}\frac{d^3\sigma_{\text{l.c.}}^{(2)}}{d\Omega_+ d\Omega_- d\omega_1} = \frac{2e^2 q_1 q_2}{\pi^2 \omega_1^2} \Bigg\{ & \left(\frac{(\mu_p - \mu_n)}{24m}\right)^2 \frac{k q_1^2 |a_{32}|^2}{2 q_2^2} \sin^2\theta_1 \sin^2\theta_2 \\ & + \frac{f^4 q_1^2}{2k} \left| 1 - \frac{(\mu_p - \mu_n) k a_{32}}{12 m f^2 q_2} \cos\theta_2 \right|^2 \cos^2\theta_1 \\ & - \frac{(\mu_p - \mu_n) f^2 q_1^2 |a_{32}|}{48 m q_2} \left| 1 - \frac{(\mu_p - \mu_n) k a_{32}}{12 m f^2 q_2} \cos\theta_2 \right| \\ & \times \sin 2\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \Bigg\}\end{aligned} \tag{7}$$

The superscripts (1) and (2) in each case denote non-spin-flip and spin-flip, cross-sections respectively. We notice the angular dependence in the case of right circularly polarised photon is much simpler than for left circularly polarised photons.

The negative pions from right circularly polarised photons are distributed as $A \cos^2\theta_1$ while those from left circularly polarised photons are distributed according to the law $A + B \cos^2\theta_1$, for the case when there is no spin-flip of the nucleon. If there is spin-flip the angular distribution is of the form $A \sin^2\theta_1$, or $A + B \cos^2\theta_1$ according as the incident photon is right or left circularly polarised.

If we are interested in the distribution of the positive pions we notice that the cross-section is proportional to $\sin^2\theta_2$ for an incident beam of right

circularly polarised photon while a beam of left circularly polarised ones yields an angular distribution of the type $A + B\cos\theta_2 + C\cos^2\theta_2$ and this is so for both the cases of spin-flip and non-spin-flip of the nucleon. These features can readily be checked against experiment.

3. Photo-Production Cross-Section for $(\pi^+\pi^0)$ Pairs from Polarised Nucleons

The complete amplitude for this case is given by

$$F(\pi^+\pi^0) = \frac{(4\pi)^{3/2} f}{(8\omega_1\omega_2 k)^{1/2}}\left[\frac{\sigma\cdot q_1\tau_3}{\omega_1}\left\{\frac{(\mu_p-\mu_n)\,e a_{32}}{4mfq_1^3}\cdot\left[\frac{1}{\sqrt{2}}(\tau_-\tau_3+\tau_3\tau_-)\right.\right.\right.$$

$$\left.-\frac{\sqrt{2}}{3}\tau_-\tau_3\right]\Big[2q_2\cdot(k\times\lambda)-i\sigma\cdot\big(q_2\times(k\times\lambda)\big)\Big]$$

$$+\frac{ief}{\sqrt{2}}(\tau_-\tau_3-\tau_3\tau_-)\left[\sigma\cdot\lambda+\frac{2\sigma\cdot(k-q_2)\,(\tau q_2\cdot\lambda)}{(k-q_2)^2+1}\right]\Big\}$$

$$-\frac{\sqrt{2}\sigma\cdot q_2\tau_-}{\omega_2}\frac{a_{31}(\mu_p-\mu_n)\,e}{6mfq_2}\big(2q_1\cdot(k\times\lambda)$$

$$\left.-i\sigma\cdot(q_1\times(k\times\lambda))\big)\right] \tag{8}$$

where

$$a_{31} = \frac{e^{i\delta_{31}(q_1)}\sin\delta_{33}(q_1)}{q_1}. \tag{9}$$

The various amplitudes are given by

$$F_{r.c.}^{(1)}(\pi^+\pi^0) = \frac{(4\pi)^{3/2}\,e\sqrt{k}\,(\mu_p-\mu_n)}{8m\sqrt{2}\,\omega_1\omega_2}\left[\frac{2q_2a_{31}\,e^{i\phi_1}\sin\theta_1\cos\theta_2}{\omega_2 q_1}\right.$$

$$\left.-\frac{q_1a_{32}\,e^{i\phi_2}\sin\theta_2\cos\theta_1}{\omega_1 q_2}\right] \tag{10}$$

$$F_{r.c.}^{(2)}(\pi^+\pi^0) = \frac{(4\pi)^{3/2}\,e\sqrt{k}\,(\mu_p-\mu_n)}{8m\sqrt{2}\,\omega_1\omega_2}\left[\frac{2q_{2+}a_{31}\,e^{i\phi_1}\sin\theta_1}{\omega_2 q_1}\right.$$

$$\left.-\frac{q_{1+}a_{32}\,e^{i\phi_2}\sin\theta_2}{\omega_1 q_2}\right] \tag{11}$$

$$F_{l.c.}^{(1)}(\pi^+\pi^0) = \frac{(4\pi)^{3/2} e}{\sqrt{\omega_1\omega_2}}\left[\frac{\sqrt{k}\,(\mu_p-\mu_n)}{24m}\left\{\frac{q_1 a_{32}\, e^{-i\phi_2}\sin\theta_2\cos\theta_1}{\sqrt{2}\,\omega_1 q_2} - \frac{\sqrt{2}\,q_2 a_{31}\, e^{-i\phi_1}\sin\theta_1\cos\theta_2}{\omega_2 q_1} - \frac{2q_{2-}a_{31}\cos\theta_1}{\omega_2 q_1}\right\} - \frac{f^2 q_{1-}}{2\sqrt{k}\,\omega_1}\left\{1-\frac{(\mu_p-\mu_n)\,k a_{32}\cos\theta_2}{12mf^2 q_2}\right\}\right] \quad (12)$$

$$F_{l.c.}^{(2)}(\pi^+\pi^0) = \frac{(4\pi)^{3/2} e}{\sqrt{\omega_1\omega_2}}\left[\frac{\sqrt{k}\,(\mu_p-\mu_n)}{24m}\left\{\frac{q_{1+}a_{32}\, e^{-i\phi_2}\sin\theta_2}{\sqrt{2}\,\omega_1 q_2} - \frac{2\,a_{31}\,q_2\cos\theta_1\cos\theta_2}{\omega_2 q_1} - \frac{\sqrt{2}\,a_{31}q_{2+}\,e^{-i\phi_1}\sin\theta_1}{\omega_2 q_1}\right\} - \frac{f^2 q_1}{2\omega_1\sqrt{k}}\left\{1-\frac{(\mu_p-\mu_n)\,k a_{32}\cos\theta_2}{12\,mf^2 q_2}\right\}\cos\theta_1\right]. \quad (13)$$

The subscripts 1 and 2 refer to the neutral and positive pions respectively. The superscripts refer as before to the non-spin-flip and spin-flip amplitudes. q_+ and q_- are given by

$$q_+ = \frac{q_x + iq_y}{\sqrt{2}}\,; \qquad q_- = \frac{q_x - iq_y}{\sqrt{2}}\,. \quad (14)$$

The differential cross-sections for the case of right circular polarisation of the incident photon are given by

$$\frac{d^3\sigma_{\gamma.c.}^{(1)}(\pi^+\pi^0)}{d\Omega_+\,d\Omega_0\,d\omega_1} = \frac{e^2(\mu_p-\mu_n)^2 k}{64\pi^2 m^2}\left[q_1{}^3|a_{32}|^2\cos^2\theta_1\sin^2\theta_2 + \frac{4q_2{}^3|a_{31}|^2\cos^2\theta_2\sin^2\theta_1}{\omega_2{}^2 q_1} - \frac{q_1 q_2\,|a_{31}|\,|a_{32}|\cos(\phi_1-\phi_2)\sin 2\theta_1\sin 2\theta_2}{\omega_1\omega_2}\right] \quad (15)$$

$$\frac{d^3\sigma_{\gamma.c.}^{(2)}(\pi^+\pi^0)}{d\Omega_+\,d\Omega_0\,d\omega_1} = \frac{e^2 k(\mu_p-\mu_n)^2}{64\pi^2 m^2}\left[\frac{q_1{}^3|a_{32}|^2}{2\omega_1{}^2 q_2} + \frac{2|a_{31}|^2 q_2{}^3}{\omega_2{}^2 q_1} - \frac{2|a_{31}|\,|a_{32}|\,q_1 q_2}{\omega_1\omega_2}\right]\sin^2\theta_1\sin^2\theta_2 \quad (16)$$

We refrain from giving the expressions for the case of left circularly polarised photons as they are quite formidable in length. Here again we notice that the angular dependence for the case of right circular polarisation is very much simpler than for the case of left circular polarisation. The positive pions arising from right circularly polarised photons with or without spin-flip for the nucleon are distributed according to the law $A + B \cos^2 \theta_2$. For left circularly polarised photons the law of distribution is $A + B \cos \theta_2 + C \cos^2 \theta_2$ for both the cases.

In conclusion, we wish to express our indebtedness to Professor Alladi Ramakrishnan and Messrs. N. R. Ranganathan and R. Vasudevan for stimulating discussions.

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